

Restricted open-shell Hartree-Fock equations.

Clearly there are many other wavefunctions that one might be interested in that are not a closed shell singlet or an unrestricted open shell that can be written as a single determinant. For example one could have a high spin triplet where the N_β spin orbitals have the same spatial form as the first $N_\alpha - 2$ α spin orbitals. These wavefunctions are called restricted open-shell Hartree-Fock functions because of the restrictions on the spatial functions. In this case one could find a single unitary transformation that would diagonalize the Lagrangian multiplier matrix associated with the N_β spin orbitals and the $N_\alpha - 2$ α spin orbitals but one would still have off-diagonal elements of the λ^α matrix that must be chosen to insure that the two open shell orbitals are orthogonal to the doubly occupied spatial orbitals. Sometimes this orthogonality can be insured by symmetry as in the ${}^3\Sigma_g^-(m_s = 1)$ state of linear methylene. In this state the two open shell electrons are in π_x & π_y spatial orbitals that are orthogonal to all other spatial orbitals. If, however, one bends methylene into C_{2v} symmetry one of the π orbitals becomes a_1 symmetry and is no longer orthogonal to the other a_1 orbitals. The Hartree-Fock equations for these restricted open shell wavefunctions are difficult to write down in general because of the different ways one can deal with the Lagrangian multipliers. Roothaan (Reviews of Modern Physics, 179, **32**, 1960) has considered a few special cases for diatomics and atoms.